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Small-scale experiments of self-sustaining decomposition of NPK fertilizer and application to the events aboard the *Ostedijk* in 2007

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Abstract

Small-scale experiments to investigate the self-sustaining decomposition (SSD) behaviour of NPK 16.16.16 fertilizer have been undertaken. These experiments show that this material will undergo self-sustaining decomposition and are used to give insight into the behaviour of the reaction. A three-step decomposition process is observed leading to a self-sustained reaction reaching temperatures of 200–350°C. The measured heat of reaction is 0.73–1.8 MJ·kg⁻¹. Measurements are applied to the events that occurred aboard the ship *Ostedijk* in 2007 in which a SSD reaction occurred. The mass loss rate from the cargo was calculated to range from approximately 0.5 kg·s⁻¹ on the first day to 12 kg·s⁻¹ on the last day. From this measurement, the maximum fire size was estimated to be in the range 5.8–29 MW.

Keywords: Ammonium nitrate, ship fire, thermal runaway

1. Introduction

Self-sustaining decomposition (SSD) is the phenomenon in which a locally initiated decomposition reaction spreads through the mass of a material. This phenomenon has been reported to occur in inorganic fertilizers and other materials with a high ammonium nitrate fraction. Other materials, such as peroxides, are also known to undergo exothermic decomposition [1].

Self-sustaining decomposition incidents can be initiated by self-heating or external heat sources. Self-heating is the phenomenon in which the temperature in a body of material rises due to heat being generated by some process taking place within the material. If this heat cannot be lost to the surroundings at a rate greater than that at which it is generated, then a thermal runaway may occur [2]. Self-heating of fertilizers is promoted when large quantities of material remain undisturbed for a long time e.g. in bulk storage or transportation, or if there is contamination with organic material with which ammonium nitrate will start to react directly at around 100°C [3]. Local external heat sources (e.g. hot work, hot surfaces and embers) can also initiate a SSD [4].

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Large SSD events are rare with one occurring worldwide on average every three years [4]. The consequences can be severe with direct casualties, formation of toxic plumes and explosions [4, 5]. Incidents involving SSD of fertilizers include warehouses in Cartagena, Spain in 2002, on the Humber coast in north-east England in 1993 and in Nantes, France in 1987 [5, 6]. These incidents were initiated by relatively small heat sources (e.g. electric lamps or faults in electric equipment) but resulted in the formation of large, toxic plumes. Kiiski [4] gives a review of eleven SSD incidents dating back to 1962 and Marlair et al. [5] summarize seven incidents dating back to 1972.

2. The *Ostedijk* and the incident timeline

In February 2007, 6012 tonnes of NPK (nitrogen, phosphorous and potassium) fertilizer cargo aboard the *Ostedijk* underwent a self-sustaining decomposition which lasted for seven days destroying part of the cargo and compromising the ship. The incident took place off the north-west coast of Spain while the vessel was en route from Porsgrunn, Norway to Valencia, Spain. A detailed timeline of events is available in [7]. The decomposition occurred in Cargo Hold Two which contained 2,627 tonnes of fertilizer.

The incident was closely followed by the Spanish media (see [7] for full details), which provided good photographic evidence of the evolution of the plume size. The plume was seen to grow from about 0.5 m diameter to greater than 50 m over five days. Although the composition of the plume is unknown, it is likely that it contained nitrogen, nitrous oxides, water vapour, and ammonium and chlorine compounds, which are products typical of NPK fertilizer decomposition [6, 8]. Thermal imaging deployed by emergency personnel measured surface temperatures of the cargo to be in excess of 175°C [7]. Heat losses from the surface mean that the inside of the cargo must have been at temperatures significantly higher than this.

Initial fire-fighting aboard the *Ostedijk* utilized an auxiliary ship to cool the outside of the hold with water jets. This started on the fourth day but proved ineffective in controlling the fire. On the fifth day, specialist salvors boarded the vessel and used localized application of water to cool the interior of the cargo. The plume prior to the commencement of extinguishing can be seen in Fig. 1. On the seventh day, the fire was declared extinguished and the vessel was allowed to reach port at Bilbao. The cargo after suppression can be seen in Fig. 2, which suggests that approximately two thirds of cargo in Hold Two was affected [9].

The International Maritime Organisation described the event as a fire which “broke out... evidently due to cargo decomposition” [10]. Meanwhile, the official standing of the Spanish authorities was that the incident was a self-sustaining fermentation reaction, which presumably refers to the phenomenon of self-sustaining decomposition [7]. This hypothesis is confirmed by analysis of the photographic evidence, reports from maritime agencies and results from small-scale laboratory experiments reported in this paper.

3. The cargo on board the *Ostedijk*

The cargo was inorganic, mineral fertilizer NPK 15.15.15 manufactured in Norway [8]. The naming convention of fertilizers means that this material contains the equivalent of 15% nitrogen (as ammonium and nitrate salts), 15% phosphorous pentoxide (as



Fig. 1. The *Ostedijk* on 21st February (the 5th day) after the hold was opened and before specialized fire-fighting activities had commenced. Derived from photograph courtesy of Agencia EFE [11]

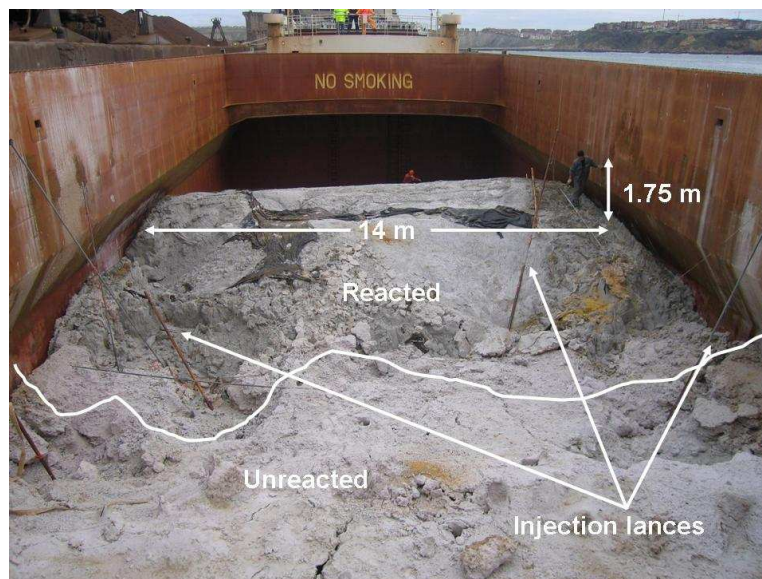
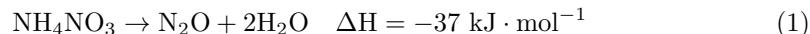


Fig. 2. Photograph of inside the cargo hold prior to unloading. The demarcation between reacted and unreacted regions as well as the water lances used for fire-fighting can be seen. Picture courtesy of Ministerio de Fomento, Spain.

phosphates) and 15% potassium oxide (as potassium chloride and potassium oxide) on a mass basis. The remaining portion of the fertilizer consists of micronutrients (magnesium, sulphur, calcium, etc) and anticaking agents. The material is of a granular nature with a bulk density in the range 900–1,200 kg·m⁻³ and particle diameter in the range 2–4 mm.

Ammonium nitrate is commonly found in fertilizers because it incorporates nitrogen in the forms readily taken up by crops (i.e. ammonium and nitrate ions). However, ammonium nitrate is capable of undergoing exothermic decomposition reactions upon exposure to a heat source [3]. Exothermic decomposition of pure ammonium nitrate begins around 200–230°C [12] and it has been suggested that it follows the general reaction described in eq. (1). A further exothermic decomposition reaction which takes place at temperatures above 230°C is presented in eq. (2) [12].



3.1. Assessing the hazard of SSD

Ammonium nitrate containing fertilizers are classified according to their propensity to undergo self-sustaining decomposition [13]. This is determined by the Trough Test as set out in the UN Recommendations on the Transport of Dangerous Goods [14]. In this test, a mesh trough of dimensions 150×150×500 mm³ is filled with the fertilizer to be tested and heated at one end. The heating is either by a 250 W electric heater or gas burners capable of heating a 1–3 mm thick steel plate to between 400 and 600°C. Heat is applied until decomposition is established and propagation of the front over 30–50 mm is observed (in some cases it may be necessary to continue heating for over two hours). The position of the decomposition front 20 min after heating has been stopped is noted. The position of the front can be determined either by thermocouple readings or differences in colour.

The classifications state that if propagation of the decomposition continues throughout the substance after heating has been stopped, the fertilizer is considered capable of self-sustaining decomposition, and that if propagation does not continue throughout the substance, the fertilizer is considered to be free of the hazard of self-sustaining decomposition. The NPK 15.15.15 aboard the *Ostedijk* was deemed to be free from the hazard of SSD.

Though not the objective of this paper, it is important to highlight some of the limitations of the test. The limitation of the trough test is that it is conducted on the centimetre scale whereas in reality, SSD accidents occur on the metre scale. This change in scale means that it is not possible to apply the Trough Test results to real-scale applications. Additionally, the ignition protocol in the test is poorly defined and the test only gives a ‘yes/no’ response to the occurrence of SSD under specific circumstances. This means that the test does not quantify the ability of a material to undergo SSD. Here we use the small scale propagation experiments to investigate the mechanisms of the reactions which are assumed not to be influenced by the sample size.

3.2. Decomposition mechanisms of ammonium nitrate-based fertilizers

The decomposition chemistry of ammonium nitrate containing fertilizers differs from that of pure ammonium nitrate (eqs. (1) and (2)), due to the presence of other compounds (especially chlorides) in the aggregate which act to alter the reaction pathway and thermal properties of the material. Public literature relating to these reactions is scarce and few details are published, however reaction mechanisms are presented by Kiiski [4] along with the following observations:

1. NH_4^+ and NO_3^- ions and a catalyst (commonly Cl^-) must be present within a small volume
2. A solid matrix must be present or formed during decomposition such that heat can be trapped and transferred to the reaction zone
3. Sufficient heat must be liberated to overcome heat losses and allow the reaction to propagate

3.2.1. Non-catalysed decomposition

The global non-catalysed reaction mechanism is a chain reaction which goes to completion and proceeds only if there is sufficient heat to maintain the decomposition [12]. The initial step involves the melting and dissociation of ammonium nitrate (NH_4NO_3) to form ammonia and nitric acid (NH_3 and HNO_3) which further decompose to N_2 , N_2O , NO_x and NO_xCl [12].

3.2.2. Catalysed decomposition

SSD of fertilizers is generally by the chloride catalysed mechanism. In this case, the decomposition is mainly that of nitric acid (HNO_3) which is formed during the endothermic dissociation of ammonium nitrate NH_4NO_3 [4]. The reaction is initiated by the formation of nitric and hydrochloric acids which undergo a chain reaction with chloride ions acting as a catalyst producing N_2 , N_2O , NO_2 and H_2O . The temperature must be in excess of 300°C to allow completion [4].

These mechanisms are complex, result in the formation of many intermediate products and are too complicated for simple analysis. In this work, a simplified framework based on laboratory observations will be proposed for use in post-event analysis (see Section 5).

4. Laboratory experiments

Small-scale experiments were carried out to investigate the decomposition behaviour of NPK fertilizer and develop a reaction framework. Experiments were carried out using NPK 16.16.16, a blend which is deemed to be similar in nature (i.e. thermal properties and composition) to that aboard the *Ostedijk* (density in the range $1,000\text{--}1,100\text{ kg}\cdot\text{m}^{-3}$ and particle size $2\text{--}4\text{ mm}$). This was due to NPK 15.15.15 being available only in industrial quantities not suitable for laboratory experiments in the UK. Since this paper aims to give an outline of the decomposition framework and not a detailed kinetic study, these materials are sufficiently close in properties and composition to draw useful conclusions [15, 16]. Three experimental methods were used: bench-scale experiments where the sample is heated with an electrical coil [17], thermogravimetric analysis [18] and experiments in the Fire Propagation Apparatus (FPA) [19]. The experimental findings are

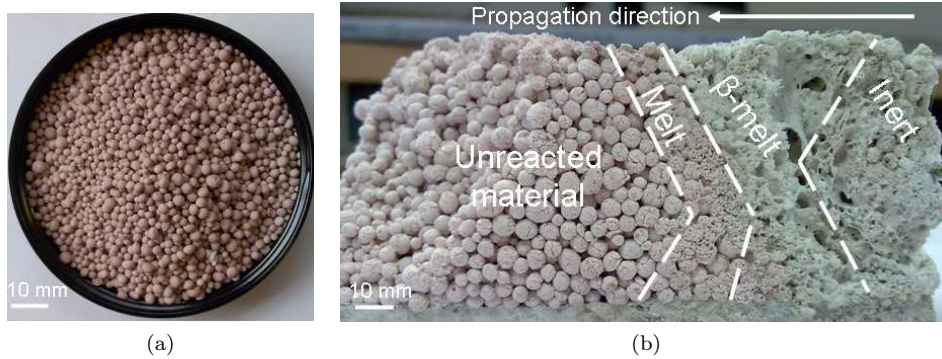


Fig. 3. (a) Unreacted fertilizer granules and (b) cross section showing partially reacted sample with 4 phases visible (see section 4.1)

applied to the case of the *Ostedijk* in Section 5. Fig. 3a shows the granular nature of the unreacted material.

4.1. Propagation experiments

Experiments were performed in a configuration similar to the Trough Test using a box constructed from insulation board. The box had dimensions of $100 \times 100 \times 50 \text{ mm}^3$ and was covered with aluminium foil. Thermocouples were placed on the igniter and in two rows in the sample at distances of 30 and 60 mm from the igniter to monitor ignition and propagation. Coiled Nichrome wire was used as the heat source for ignition. 150 W of power was applied during the whole experiment. This set-up was used to provide an insight into the ignition of SSD and the conditions necessary for propagation of the decomposition front. Figure 3b shows the decomposition occurring in three steps. The unreacted material melts, undergoes reaction to form an intermediate product (β -melt), before undergoing further reaction to form an inert product.

Figure 4 shows the temperature evolution of the three thermocouple locations. Below 200°C , melting occurs and there is little offgassing. The exothermic reaction steps occur between ~ 200 and 350°C with initial offgassing of an orange hue which turns white as the reaction progresses. The upper temperature limit observed in Fig. 4 is affected by heat transfer from the igniter, which increases the local temperature above that of the reaction.

The reacted samples showed significant mass loss in the reaction zone. There is also a colour gradient from the pink granules of the virgin material, a pink molten phase with some particle agglomeration and a grey phase (β -melt) which is characterised by pores 2–6 mm in diameter. The final, inert phase has an off-white appearance and a density of around $340 \text{ kg}\cdot\text{m}^{-3}$. This phase forms a matrix in which small pores approximately 1–3 mm in diameter and larger pores up to several cm (see Fig 3b).

Mass loss of 49% is measured when reaction spreads throughout the reaction zone. The spread rate (calculated using the time when the temperature at a thermocouple exceeds 200°C) was found to be of the order of $10 \text{ mm}\cdot\text{min}^{-1}$. This may be a function of the sample size, however further investigation is beyond the scope of this paper.

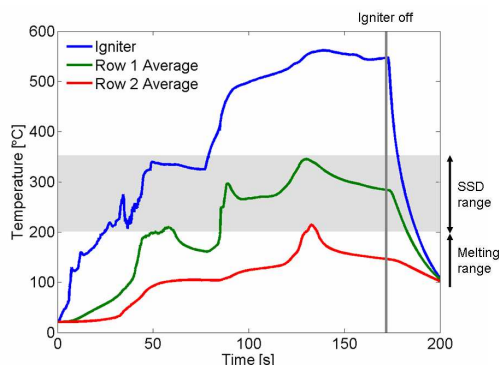


Fig. 4. Temperature traces for the propagation experiments. The igniter is turned on at $t = 0$ and is switched off at after 172 s leading to rapid cooling. The temperatures are averages of 2 thermocouples in each row; row 1 is located 50 mm and row 2 90 mm from the igniter at a depth of 25 mm.

The propagation experiments do not allow all the details of the decomposition to be observed. In order to gain a better understanding of the reaction paths and exothermicity, further experiments on SSD reactivity were carried out.

4.2. Thermogravimetric analysis (TGA)

Thermogravimetric tests [20] allow measurement of the mass loss of a sample as a function of the sample temperature. The resulting mass loss curve allows the reactions occurring during the decomposition of the material to be characterized.

Figure 5 shows the relationship between mass and temperature for 10 mg samples of fertilizer, subject to different heating rates and atmospheres. Heating rates of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ and $20^{\circ}\text{C}\cdot\text{min}^{-1}$ were used in an air atmosphere and $10^{\circ}\text{C}\cdot\text{min}^{-1}$ was used in a nitrogen atmosphere up to 500°C . In each case, the following trend is seen: up to 200°C there is very little mass loss. During this time, the sample is melting, which is an endothermic process. Between 220 and 260°C there is a strong reaction resulting in 42–48% mass loss, which is followed by a period of slow mass loss up to 500°C . The total mass loss is approximately 45–52%. There is good agreement between the temperatures at which the mass loss occurs in these experiments and the reaction temperatures observed in the propagation experiments (Section 4.1). There is also good agreement in the mass losses with a value of approximately 50% in both sets of experiments.

Figure 6 shows the result of differential thermal analysis (DTA) of the samples. The temperature difference between the sample and an inert reference in the TGA apparatus is measured to give a representation of the heat release of any reactions occurring. Positive temperature differences are a result of exothermic reactions with net heat release, while negative temperature differences arise due to endothermic reactions.

The peak in heat release coincides with the peak in mass loss at temperatures between 220 and 260°C . As the difference is positive, the reaction is exothermic. The difference before and after the peak can be attributed to endothermic reactions such as melting and drying of the fertilizer or further degradation of the product species. The similarity of the curves in Figs 5 and 6 under the air and inert environments means that the reaction does not consume oxygen. Small differences in mass loss and heat release can be attributed

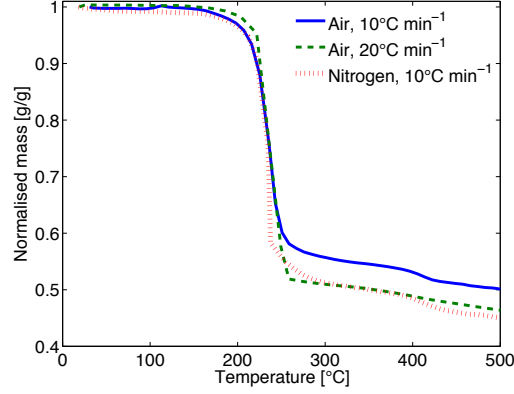


Fig. 5. Mass versus temperature at heating rates of 10 and 20°C/min in air and 10°C/min in nitrogen for the TGA experiments. Mass loss is not affected by heating rate or environment, with the majority occurring at 220–260°C in agreement with Fig. 4.

to experimental uncertainties, such as sample preparation and variations in heating rate. Units in Fig. 6 are in μV , representing the temperature difference between the sample and an inert reference material and therefore the heat release.

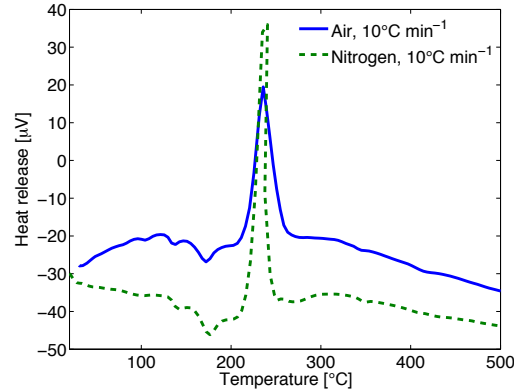


Fig. 6. DTA measurements for fertilizer in air and nitrogen environments. Maxima represent exothermic reactions and minima endothermic reactions. Note the large exothermic reaction at 220–260°C which is in agreement with temperatures observed in Fig. 4. The results can not be interpreted quantitatively due to differences in apparatus and sample preparation, and only provide qualitative estimation of the reactions occurring.

4.3. Reactivity experiments

The Fire Propagation Apparatus (FPA) [21] was used to investigate the decomposition behaviour and determine the mass loss, gas emissions and heat released rate (HRR) during the SSD process. The FPA is a calorimeter which allows the heat released when a material decomposes to be measured. The decomposition is initiated by a uniform radiative heat flux on the surface of a sample. Product gas composition, flow and temperature

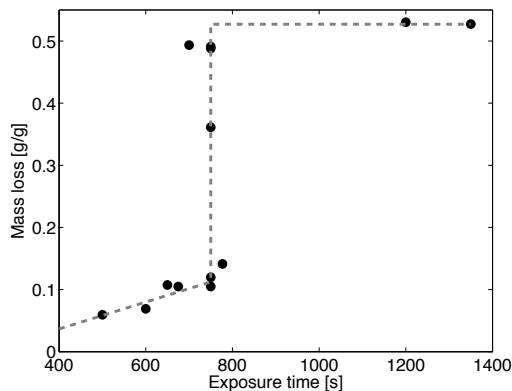


Fig. 7. Mass loss of samples as a function of the exposure time to the ignition source. The sharp transition at 750 s indicates the onset of SSD.

can then be measured in the exhaust duct. In this work, the heat release of the fertilizer is measured using the temperature and flow rate of gas in the exhaust duct.

Samples of 130 g of fertilizer were placed in a sample holder of diameter 100 mm, forming a layer 25 mm deep. The samples were exposed to an external radiant heat flux of $20 \text{ kW}\cdot\text{m}^{-2}$ for various lengths of time. All samples underwent decomposition and, for exposure times greater than 750 s, reached self-sustaining decomposition as seen in Fig. 7. If the exposure time was shorter than this then the mass loss was observed to increase with increasing exposure time up to mass loss of around 15%. After this time, significantly higher mass losses of up to 53% are observed with a lower dependence on exposure time.

Figure 8a shows the mass loss as a function of time for three samples exposed to the heat flux for 650 s, 750 s and until the reaction is completed after approximately 1,250 s. The non-self-sustaining reaction for heat flux exposure of 650 s can be seen as well as the self-sustaining behaviour for exposure times greater than 750 s. The small mass loss early in the experiment is due to the reaction in a thin layer of material on the surface of the sample. For samples where the exposure time was less than 750 s, the mass loss rate is observed to rapidly decrease to zero after the external heat flux is switched off.

Three distinct regimes of mass loss are apparent in Fig. 8b which shows six repeats of the same experiment (i.e. incident heat flux of $20 \text{ kW}\cdot\text{m}^{-2}$ for 750 s): 1) low mass loss rate during the heating phase (0–300 s); 2) moderate mass loss rate (300–700 s); and 3) high mass loss rate (700–1500 s). The reactive fraction of the sample was completely consumed after ~ 1500 s. The mass loss rates in the second and third regime are $0.035\text{--}0.045$ and $0.06\text{--}0.11 \text{ g}\cdot\text{s}^{-1}$ respectively. Only the third regime is self-sustaining and truly represents the SSD phenomenon. The data after the heat flux is switched off shows more variability suggesting that this stage is more sensitive to small uncontrolled external factors.

Total mass loss measurements indicate that a fraction of the fertilizer is not involved in the reaction and remains in the holder as a condensed phase. This remaining material accounts for $52\pm 3\%$ of the initial mass and, once cooled, has a porous structure white in colour and is inert, suggesting that it is of mineral origin as described

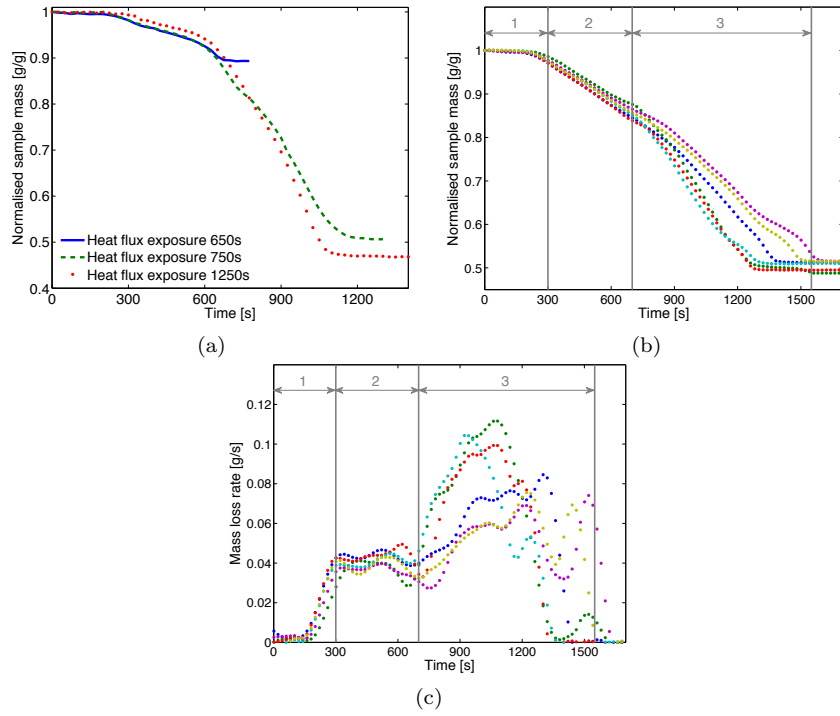


Fig. 8. (a) Normalized mass loss for tests with heat flux exposure of 650 s, 750 s and full exposure until reaction completion, 1250 s. The increased mass loss rate and final mass loss for the 1,250 s exposure are due to the additional heat insult received by the sample. (b) Normalized mass loss regimes observed in six repeat experiments each subject to a 750 s, $20 \text{ kW}\cdot\text{m}^{-2}$ exposure. Note the differences in mass loss rate after the external heat flux is switched off. (c) Mass loss rates for the experiments shown in (b).

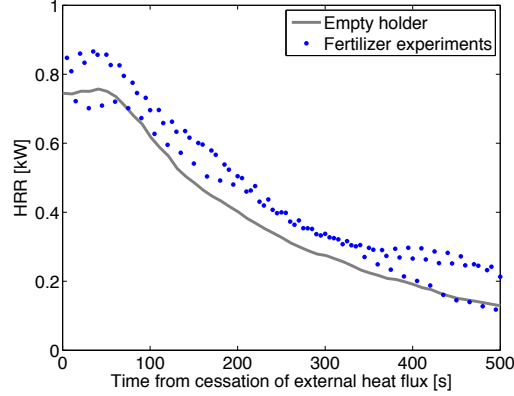


Fig. 9. The increased heat released for experiments with fertilizer (blue) and the background (black). Time starts after the cessation of the heat flux at 750 s.

in Section 4.1. This inert fraction is in agreement with previous measurements of 49% in the propagation experiments and 45–25% in the TGA.

Additionally, the FPA allows measurement of O_2 , CO and CO_2 concentrations in the product gases and the convective heat release rate. Analysis of the product gases shows that these remain at ambient levels during the experiment, indicating that the SSD reaction does not produce or consume O_2 , CO or CO_2 and thus does not contain any carbonaceous material. Figure 9 shows the heat released by the reaction against an empty, reference holder. The heat release is calculated by measuring the temperature and flow of gases in the exhaust duct.

Figure 9 shows data after the external heat flux is switched off, i.e. after 750 s of exposure corresponding to the third mass loss regime. The SSD is weakly exothermic with the heat released ranging from 0.08 to 0.11 kW above the background. To find the heat of reaction, the heat released is divided by the mass loss rate. From above, this is in the range 0.06–0.11 $g \cdot s^{-1}$. Therefore, the heat of reaction is 0.73–1.8 $MJ \cdot kg^{-1}$ —approximately 15 times lower than that of wood [22].

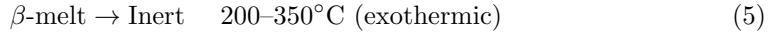
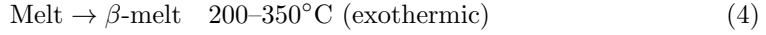
4.4. Proposed decomposition framework

From the experimental measurements and observations, a three-step decomposition framework with four species is proposed. Analysis of the samples after reaction in the two experimental series shows four species: virgin material, molten material, molten material which has partially undergone reaction (β -melt) and inert matrix (see Fig. 3b).

The minimum exposure time seen in Fig. 7 shows that there is a minimum amount of material which must be heated in order to initiate self-sustaining decomposition. The first step of the proposed framework is the melting of the fertilizer, which is endothermic. This is correlated to mass loss regime 1 in Section 4.3. This molten material undergoes reaction to form an intermediate product (β -melt) which then undergoes further reaction to form the inert product. This corresponds to mass loss regime 2 in Section 4.3. After enough heat has been supplied, the reaction front is large enough that the heat released is sufficient to promote melting and heating of the virgin fertilizer up to the reaction

temperature, and the reaction can propagate unaided (this is what happens in mass loss regime 3).

The proposed reaction framework is as follows:



5. Application to the *Ostedijk* event

These results can be applied to the events aboard the *Ostedijk* to give further insight, however it is not within the scope of this paper to comment on the possible cause and origin of the ignition source.

Photographic evidence in the Spanish media of the 2007 event aboard the *Ostedijk* clearly shows the development of the plume from the cargo hold [7]. Estimating the mass of cargo lost in the plume from photographs gives an indication of the size and growth rate of the SSD and, using data from the laboratory tests, the heat released can be estimated.

The plume flow rate was calculated using two methods. For the second, third and fourth days (no data were available for day 1), wind speed from historical records [23] and angle of plume deflection were used to resolve for the velocity vector normal to the ship deck, as in eq. 6 where θ is the angle between the plume centreline and the line normal to the deck surface. Estimating the vent diameter in the cargo cover, through which the gas flowed, the flow rate could then be obtained. The angle of plume deflection varies from 10° from the horizontal on the first day to 40° on the fourth day. The volumetric flow rate could be converted to a mass flow by multiplying by the plume density at the gas temperature (taken to be 200°C , as this is below the decomposition temperatures found in Section 4.2) estimated to be $0.74 \text{ kg}\cdot\text{m}^{-3}$ (assuming the plume has the same molecular weight as air). On the fifth day, the flow rate was estimated using Gaussian plume theory [24], as described by eq. 7, as opening the holds had lead to a much larger, well defined plume suitable for such analysis. In eq. 7, C is the gas concentration along the edge of the plume (as this is well defined in the photographs, a trace concentration of 1×10^{-6} was chosen), u is the wind speed ($6 \text{ m}\cdot\text{s}^{-1}$ from historical data [23]), $\sigma_y = 0.08x(1 + 0.0001y)^{-0.5}$ and $\sigma_z = 0.06x(1 + 0.0001x)^{-0.5}$ are the lateral and vertical dispersion coefficients respectively, H_e is the elevation of the plume centreline above ground and z is the height above ground of the region of interest.

$$\text{plume velocity} = \frac{\text{wind speed}}{\tan \theta} \quad (6)$$

$$\text{Release rate (kg}\cdot\text{s}^{-1}) = \frac{2\pi\sigma_y\sigma_zCu}{\exp(-\frac{1}{2}(\frac{z}{\sigma_y})^2)(\exp(-\frac{1}{2}(\frac{z-H_e}{\sigma_y})^2) + \exp(-\frac{1}{2}(\frac{z+H_e}{\sigma_z})^2))} \quad (7)$$

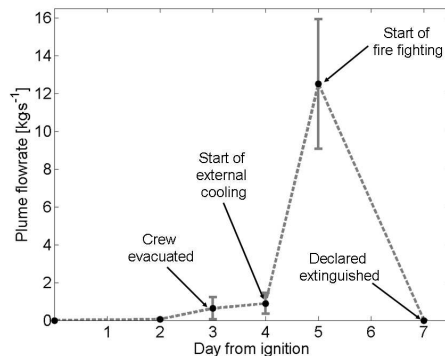


Fig. 10. Estimated plume flow rates during the event. The error in day 2, 3 and 4 arises from using different images to calculate flow rate, meanwhile the error in day 5 arises due to the sensitivity of eq. 7 the input parameters. The fire was declared extinguished on day 7. Other events are indicated.

Applying the results from the experimental investigations to the events aboard the *Ostedijk* allows us to draw some additional conclusions regarding the accident. The observed orange plume on the third day corresponds well to those observed in the early stages of our experiments and would indicate that the fire was propagating through the cargo. The white plume observed during most of the event would indicate sustained propagation with temperatures between 200 and 350°C in the bulk of the material and is in agreement with the temperature of 175°C on the surface of the cargo as reported in [7].

Combining the plume analysis with the measured heat of reaction allows estimation of the heat release rate from Cargo Hold Two of the *Ostedijk*. The flow of gases estimated in Fig. 10 equals the mass loss from the cargo hold due to the SSD. Thus, multiplication of the flow rate by the heat of reaction gives the energy released. By this calculation, it is estimated that the amount of energy released by the SSD was of the order of 0.4–0.9 MW the first day and grew to between 5.8 and 29 MW on the fifth day. These calculations are based on the heat of reaction as calculated in Section 4.3.

6. Conclusions

The small-scale experiments performed have given insight into the SSD behaviour of inorganic fertilizers. From the experiments, a minimum temperature of 200°C is required to initiate SSD and the steady-state reaction temperature in the bulk of the material ranges between 200 and 350°C. The propagation process has been characterized and a phenomenological decomposition framework is proposed based on the experimental observations.

The analysis of the event has further indicated that the bulk cargo of NPK fertilizer aboard the *Ostedijk* underwent a self-sustaining decomposition reaction. The plume analysis shows rapid growth of the fire and allows estimation of the mass loss, heat release rate and the front size. Although NPK 15.15.15 is classified as a class C fertilizer (i.e. one which will not sustain decomposition in the Trough Test), the fertilizer cargo ignited and an SSD fire grew rapidly for seven days. Our analysis of NPK 16.16.16

(also Class C) indicates that it can also undergo SSD under the correct conditions. This highlights the limitations of the Trough Test and the lack of attention given to fertilizer fires by the research community.

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- [1] D. Drysdale, *An Introduction to Fire Dynamics*, John Wiley and Sons, 1998.
- [2] P. C. Bowes, *Self-heating: Evaluating and Controlling the Hazards*, Her Majesty's Stationary Office, 1984.
- [3] V. Babrauskas, *Ignition Handbook*, Fire Science Publishers, 2003.
- [4] H. Kiiski, *Self Sustaining Decomposition of Ammonium Nitrate Containing Fertilisers*, Presented at 70th International Fertiliser Association Conference, Paris.
- [5] G. Marlair, M.-A. Kordek, Safety and security issues relating to low capacity storage of AN-based fertilisers, *Journal of Hazardous Materials* 123 (2005) 13–28. doi:10.1016/j.jhazmat.2005.03.028.
- [6] A. M. Palomo, Report On The Accident At Escombreras - Cartagena ("Informe Sobre El Accidente En Escombreras - Cartagena"), *Revista de Proteccion Civil* 11, Madrid, Spain.
URL www.proteccioncivil.org/eu/DGPCE/Informacion_y_documentacion/catalogo/carpeta06/revispc11/rpc11_16.htm
- [7] R. Hadden, F. Jervis, G. Rein, Investigation of the Fertilizer Fire aboard the *Ostedijk*, *Fire Safety Science* 9 (2008) 1091–1101. doi:10.3801/IAFSS.FSS.9-1091.
- [8] Yara International, Decomposition of NPK 15-15-15 on m/v 'Ostedijk' in February 2007 - Internal Investigation Report.
- [9] Direccion General de la Marina Mercante, Personal Communication, Subdireccion General De Seguridad Martima y Contaminación, Ministerio De Fomento, Spanish Government, Madrid, Spain (2007).
- [10] Technical Group on the MEPC ON OPRC-HNS, Summary of the Incidents Involving HNS and Lessons Learnt, Tech. rep., International Maritime Organisation, accessed September 2008 (2008).
URL www.imo.org
- [11] Agencia EFE, with permission.
- [12] J. I. Kroschwitz (Ed.), *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons, 1994.
- [13] Handbook for the Safe Storage of Ammonium Nitrate Containing Fertilisers, International Fertilizer Industry Association and the European Fertilizer Manufacturers Association, 1992.
- [14] United Nations, *UN Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria*, United Nations, New York and Geneva, 2002.
- [15] Yara International, Yara Milla 16-16-16 Technical Data, Tech. rep. (Accessed October 2009).
URL http://mediabase.edbasa.com/kunder/yaraimages/agribro/agribro/agribro/j2007/m07/t16/0003350_2.pdf
- [16] Yara International, Yara Milla 15-15-15 Technical Data, Tech. rep. (Accessed October 2009).
URL http://mediabase.edbasa.com/kunder/yaraimages/agribro/agribro/agribro/j2007/m07/t16/0003350_2.pdf
- [17] G. Rein, N. Cleaver, C. Ashton, P. Pironi, J. L. Torero, The severity of smouldering peat fires and damage to the forest soil, *Catena* 74 (3) (2008) 304–309. doi:10.1016/j.catena.2008.05.008.
- [18] T. J. Ohlemiller, *SFPE Handbook of Fire Protection Engineering*, 3rd Edition, National Fire Protection Association, Quincy, MA 02269, 2002, Ch. 7, pp. 1–110–1–131.
- [19] A. Tewarson, *SFPE Handbook of Fire Protection Engineering*, National Fire Protection Association, 2002, Ch. 3-4: Generation of Heat and Chemical Compounds in Fires, pp. 3–82–3–161.
- [20] M. M. H. A. B. Morgan, *SFPE Handbook of Fire Protection Engineering*, 4th Edition, National Fire Protection Association, Quincy, MA 02269, 2008, Ch. 1-7: "Thermal Decomposition of Polymers", pp. 1–112–1–143.

- [21] M. Janssens, SFPE Handbook of Fire Protection Engineering, 4th Edition, National Fire Protection Association, Quincy, MA 02269, 2008, Ch. 3-2: "Calorimetry", pp. 3-60-3-89.
- [22] P. DiNenno (Ed.), SFPE Fire Protection Handbook, National Fire Protection Association, 2002, Ch. Appendix C.
- [23] National Severe Storms Laboratory Historical Weather Data Archives, Historical Weather Data Archive, <http://data.nssl.noaa.gov> (Accessed October 2009).
- [24] S. R. Hanna, D. Strimaitis, Workbook of Test Cases for Vapour Cloud Source Dispersion Models, 1st Edition, Center for Chemical Process Safety, American Institute of Chemical Engineers, 1989.